FIBROUS NANO-CARBON AND PREPARATION METHOD THEREOF

Technical Field

This invention relates to fibrous nanocarbons, especially to ladder-structured and pair-structured fibrous nanocarbons and the preparations of the same.

Specifically, the fibrous nanocarbons of this invention can be used as the fillers of polymer and ceramic composites, catalyst support for fuel cell, catalyst supports for organic unit reaction, gas storing materials for methane and hydrogen, anodic and conductive materials for lithium secondary battery, and electrode materials for high performance electric double layered capacitor.

Specifically, This invention relates to the ladder structured fibrous nanocarbons and the pair structured fibrous nanocarbons and its preparation method.

Background of Art

Since the discovery of carbon nanotube by Dr. Iijima in NEC Co. Ltd. (ref: S. Iijima, Nature, 354, 56 (1991)), lots of reports and patents for the preparations and applications of fibrous nanocarbons such as carbon

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nanotube and carbon nanofiber have been published.

Carbon nanotube usually has a hollow fibrous nano-structure with the diameter of larger than 0.4nm. Carbon nanotube has a structure of concentrically-stacked hexagonal planes which are almost aligned along to the fiber axis. Single Wall Carbon Nanotube (SWNT) has most fundamental structure because it is composed of only one concentric hexagonal plane, where Multi Wall Carbon Nanotube (MWNT) are usually composed of more than two concentrical hexagonal planes. SWNT has the range of diameter from 0.4 ~ 2.0 nm and MWNT has the range of diameter from 3.5-50 nm.

Three major preparation methods of Arc-discharge of carbon electric rod (ref: S. Iijima, Nature 354, 56-58 (1991); T. W. Ebbesen, P. M. Ajayan, Nature 358, 220-222 (1992)), laser-ablation methods (ref: P. Nikolaev, M. J. Bronikowski, R. Kelley Bradley, Frank Rohmund, Daniel T. Colbert, K.A. Smith, Richard E. Smalley, Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide, Chemical Physics Letters, 313(1999), 91-97), and Chemical Vapor Deposit methods (ref: G. G. Tibbetts, J. Cryst. Growth 66, 632-638 (1984); R. T. K. Baker, Carbon 27, 315-323 (1989), H. G. Tennent, Hyperion Catalysis International, Inc., US patent no. 4663230, USA, (1987)) have been mainly used for the preparation for fibrous nanocarbons among lots of synthetic processes.

Mass-production of MWNTs using CVD method has been already launched by some companies, for example, Hyperion Catalysis International Inc (ref: H. Zeng et al., Carbon, 36, 259-261(1998); Hyperion

Catalysis International Inc. WO09007023A1).

Carbon nanofibers have been classified their structures into three typical alignments of graphitic hexagonal planes such as platelet, herringbone and tubular ones (ref: N.M. Rodriguez, A. Chambers, R.T.K.
5   Baker, Catalytic Engineering of Carbon nanostructures. Langmuir 1995; 11(10): 3862-3866). Platelet carbon nanofibers showed the perpendicular alignment of graphitic hexagonal planes to the fiber axis and herringbone or feather ones did the inclined alignment with 20 – 80 degrees to the fiber axis, which can not maintain the continued tubular structures in the fibrous
10 forms like carbon nanotubes. Tubular carbon nanofiber which has the parallel alignment of graphitic hexagonal planes to the fiber axis resembles or is the same with carbon nanotube according to its definition. There may be much more varieties of fibrous structures in term of transient alignments and surface roughness.

15 Such carbon nanofibers can usually prepared by catalytic synthesis of gases or hydrocarbons over the metals that are mainly composed of metals of VI B such as Fe, Ni, Co.

Fibrous nanocarbon can be defined as a fibrous nanocarbon which has a diameter or width of 0.46 – several hundreds nano meters and aspect
20 ratios (ratio of length over diameter) of over 4. Fibrous nanocarbons can be classified into carbon nanotubes and carbon nanofibers according to the diameters or widths and structure of their fibrous forms.

Lots of patents and papers have been reported for the definitions and

preparations method of fibrous nano carbons as described above.

Exxon Research Co. reported the preparation method that fibrous nanocarbons with the length of over 1 micro-meter were prepared by the catalytic pyrolysis of carbon monoxide (CO) or hydrocarbons over the iron,

5   iron oxide or nickel catalysts in the temperature ranges of 540 – 800°C. [US patent 4565683].

Hyperion Catalytic International Inc. claimed MWNT or tubular carbon nanofibers of fibrous structured carbons which had a hollow fibril with 8-15 concentrically-stacked carbon hexagonal planes, having inner diameter of

10   around 5 nm and outer diameters of 3.5 – 70 nm. [JP 62-50000943]

R. T. K. Baker and N. M. Rodriguez reported the carbon nanofibers and their preparation methods with the surface area of 50 – 800 m^2/g. Such carbon nanofibers are prepared by the catalytic pyrolysis of hydrocarbons over the transition metals of Fe, Ni and Co in the temperature ranges of 500

15   – 750 degree C. (ref: Carbon Fiber Structures Having Improved Interlaminar Properties", United States Patent Number 5,149,584, September 2 1992, "High Performance Carbon Filament Structures", US Patent 5,415,866, May 9 1995, "Removal of Contaminants from Aqueous and Gaseous Streams Using Graphitic Filaments", US Patent 5,458,784, October 17 1995, "High

20   Performance Carbon Filament Structures", US Patent 5,618,875, April 8 1997)

Boehm, Murayama, and Rodriguez also reported the preparations of carbon nanofibers or filamentous carbons individually by the catalytic

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pyrolysis of carbon monoxide and hydrocarbons over the transition metals of Fe, Ni, and Co. (ref: Boehm, Carbon, 11, 583 (1973); H. Murayama, T. Maeda, Nature, 245,791; N.M. Rodriguez, 1993. *J. Mater. Res.* 8: 3233)).

Since the surprising hydrogen storing amounts up to 40~63 wt% has
5   been released by Baker and Rodriguez (ref: US Patent 6159538), much attention was focused on the possibility of hydrogen adsorption in carbon nanofibers and carbon nanotubes at room temperature via chemical adsorption under the high pressure over 8 MPa. The reproducibility have been tried by lots of researchers over the world so far, such high value can
10   not be still reproduced obtain. (ref: X. Chen, M. Haluska, U. Dettlaff-Wegliskowska, M. Hirscher, M. Becher, S. Roth, Mat. Res. Soc. Symp. Proc. 706 (2002) Z9.11.1; DOE Report, IEA Task 12: Metal Hydride and carbon for Hydrogen Storage 2001, Project No. C-3 – Leader: Richard Chahine (Canada), Assessment of Hydrogen Storage on Different Carbons).
15   R. Stroebel reported that carbon nanofibers adsorbed hydrogen by twice than activated carbons with the same surface area under the high pressure of hydrogen of over 10 MPa [R. Stroebel et al. J. Power Sources, 84, (1999), 221) Attention on the hydrogen adsorption of fibrous nanocarbons is still continued even through no exact explanation of the mechanism has
20   been understood.

Many results have been found for the preparation and structure of carbon nanofiber or carbon nanotube with special bamboo-like structure. The bamboo-like carbon nanofibers have been known to have the hollow nano-fibrous structure with periodically connected inner wall surface by the

graphene knobs, remaining closed inner space.

Chen et al prepared bamboo-like carbon nanofibers by the catalytic pyrolysis of ethylene over the Cu-Ni alloy over the reaction temperature of 720°C. (ref: Carbon 39 (2001) 1467–1475, Formation of bamboo-shaped
5   carbon filaments and dependence of their morphology on catalyst composition and reaction conditions, Jiuling Chen, Yongdan Li , Yanmei Ma , Yongning Qin, Liu Chang).

Kajiura et al. also reported bamboo-like carbon nanofibers obtained by the arc-discharge method. (ref: Carbon 40 (2002) 2423–2428, High-purity
10   fibrous nanocarbon deposit on the anode surface in hydrogen DC arc-discharge, Hisashi Kajiura, Houjin Huang, Shigemitsu Tsutsui , Yousuke Murakami, a Mitsuaki Miyakoshi). Their reports were limited to deal with the bamboo-like carbon nano-structure in which the closed inner space by the periodical knob of joint was blockaded by the wall of graphene sheets.

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Disclosure of Invention

The present invention was designed to solve the problems of conventional carbon nanofibers as described above, and specifically the purpose of this invention is to provide fibrous nanocarbons with ladder or
20   pair structures to be used for various fields such as pigments, inks, films, coating materials, and composites, especially with transparency.

Further, the present invention purposed to provide a high yield

preparation of the fibrous nanocarbons with ladder or pair structures to be used as a high-efficient material for overall industry, for examples, a catalyst support of fuel cells; a gas storage medium for hydrogen or methane; and an electrode or conductor in lithium secondary battery and super EDLC (Electric Double Layered Capacitor).

To achieve the aforementioned purposes, this invention discloses a ladder-structured fibrous nanocarbons, concerning a uni-modally- or bi-modally-formed fibrous nanocarbons, which is characterized by (1) the sp^2 hybrid carbon content of more than 95% per total content; (2) the interlayer spacing (d_{002}, d-spacing of C(002) profiles determined by X-ray diffraction method) of 0.3360nm~0.3800nm; (3) the (002) plane stacking of more than 4 layers and the aspect ratio of more than 20; (4) the fiber cross-section's width/thickness of 2.0nm~800nm; (5) the inclination angle of hexagonal plane alignment to the fiber axis of 0~85 degrees; and (6) carbon hexagonal planes stacking along the fiber axis, forming knots (nodes) at intervals of 5 nm ~ 100 nm, sharing partly the structure or stacking layers with the opposite side hexagonal planes and connecting periodically to each other, consequently forming ladder-like structure, wherein the inner side of the fibrous nanocarbon is open and connected to the outer space.

A pair-structured fibrous nanocarbon of this invention concerns the uni-modally or bi-modally grown fibrous nanocarbons, which is characterized by (1) the sp^2 hybrid carbon content of more than 95% per total content; (2) d_{002} of 0.3360nm~0.3800nm; (3) the (002) plane stacking of more than 8 layers; (4) the width/thickness of fiber cross-section of 2.0

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nm~800 nm; (5) the aspect ratio is more than 20; and (6) bonding of two unit fibers formed by said (1) ~ (5) features, being induced by the interaction between the two unit fibers in the beginning of formation, also leaving a uniform interval of 0.5nm ~ 30nm.

5   Also, this invention discloses preparation method of said ladder- or pair-structured fibrous nanocarbons, characterized by catalytic pyrolysis of carbon source gas or liquid, wherein said catalysts are prepared in the form of unsupported bulk or powder metals, wherein the reduction of said metals by hydrogen provides reduced forms, and simultaneously very fine metal

10   particles are obtained by roles of hydrogen or hydrogen radical during said reduction process.

Particularly, transition metals active to aforementioned carbon sources, such as Fe, Ni or Co are used as primary metals, and, in order to assist fine-particle formation of said primary metals, secondary metals

15   inactive to said carbon sources are added in 5 ~ 95wt%, providing uniformly finer metal particles, which are used as unsupported metal catalysts in this invention. Metal catalysts as prepared above are used as fibrous nanocarbon preparation catalysts, wherein the preparation of fibrous nanocarbons in this invention is attained through introduction of 3-phase

20   gas mixtures of hydrocarbons, hydrogen, and helium at 0.5 ~ 30 sccm per 1 mg catalysts, wherein said hydrogen partial pressure is selected in 2 ~ 95 v/v%, the heat treatment is performed at temperatures of 380 ~ 750°C for 2 min ~ 48 h.

Ladder- and pair-structured fibrous nanocarbons as described above

and proved by Examples in this invention have advantages of using both inner and outer surfaces for adsorption in any time, differing from bamboo-like carbon nanotubes of closed inner space or conventional carbon nanotubes which are connected to outer space just in the parts of

5 defects, partial surfaces, or tube tips formed by removal of catalysts. Therefore, ladder- and pair-structured fibrous nanocarbons in this invention enable uniform interval doping of metals or inorganic materials to said fibrous nanocarbons, developing novel applications such as gas storage of methane and so on; conventional catalyst supports; and electrical energy

10 storage.

Brief Description of Drawings

Figure 1 illustrates HR-SEM photograph of the present ladder-structured fibrous nanocarbons produced in Example 1.

Figure 2A and Figure 2B illustrate TEM photographs of

15 ladder-structured fibrous nanocarbon and enlarged image of the same.

Figure 3A and Figure 3B illustrate 30 degree tilted TEM photograph of ladder-structured fibrous nanocarbon and enlarged image of the same.

Figure 4 illustrates the structural model of fibrous nanocarbon shown in Figure 1.

20 Figure 5 illustrates HR-SEM photograph of carbon nanotube produced in Comparative Example 1

Figure 6 illustrates TEM photograph of carbon nanotube produced in Comparative Example 1

Figure 7 illustrates low magnified HR-SEM photograph of the present pair-structured fibrous nanocarbons produced in Example 3.

5   Figure 8 illustrates high magnified HR-SEM photograph of the present pair-structured fibrous nanocarbons produced in Example 3.

Figure 9A, Figure 9B and Figure 9C illustrate STM photograph, real probe scanning profile the cross-section, and conjectured profile of the cross-section of the present pair-structured fibrous nanocarbons produced 10   in Example 3, respectively.

Figure 10A and Figure 10B illustrate TEM photographs of the side and plane views of the present pair-structured fibrous nanocarbons produced in Example 3.

·   Figure   11   illustrates   HR-SEM   photograph   of   the   present 15   pair-structured fibrous nanocarbons produced in Example 4.

Figure 12 illustrates TEM photograph of the present pair-structured fibrous nanocarbons produced in Example 4.

Figure 13 illustrates the structural models of pair-structured fibrous nanocarbons in Example 3 and Example 5.

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Best mode for carrying out the Invention

The following describes fibrous nanocarbons in the present invention and preparation methods thereof. First, the overall description is given, and the details of this invention are provided by Examples, compared to Comparative Examples. In following Examples and Comparative Examples, the fibrous nanocarbons are referred as 'ladder-structured fibrous nanocarbon' when the structure resembles a ladder, and 'pair-structured fibrous nanocarbon' when the structure are formed by bonding of two unit fibers.

Ladder-structured fibrous nanocarbon

· Ladder-structured fibrous nanocarbon in this invention is not yet reported on the properties and application of the same, hence a novel material which is formed by bonding at uniform intervals, simultaneously with formation and growth of two unit carbon nanofibers, wherein the inner side of the fibrous nanocarbon is open and connected to the outer space.

As a fibrous nanocarbon, many reports have disclosed the bamboo-like carbon nanotube which is formed by periodical connection by carbon hexagonal plane stacking in some parts of the hollow core.

However, this invention discloses a ladder-structured fibrous nanocarbon which is formed by independently-grown two unit fibers' connecting as a ladder shape at uniform intervals or units in some parts of Hexagonal plane stacking comprising each fibril with the structure sharing with each other, wherein the inner space of said intervals or units is open or

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connected to the outer space.

Ladder-structured fibrous nanocarbons in this invention concerns a uni-modally- or bi-modally-formed fibrous nanocarbon, which is characterized by (1) the sp^2 hybrid carbon content of more than 95% per total content; (2) the interlayer spacing (d_{002}, d-spacing of C(002) profiles determined by X-ray diffraction method) of 0.3360nm~0.3800nm; (3) the (002) plane stacking of more than 4 layers and the aspect ratio of more than 20; (4) the fiber cross-section width/thickness of 2.0nm~800nm; (5) the 0~85 degree inclination angle of hexagonal plane alignment for each unit carbon nanofibers to the fiber axis; and (6) carbon hexagonal planes stacking along the fiber axis, forming knots (nodes) at intervals of 5 nm ~ 100 nm, sharing partly the structure or stacking layers with the opposite side hexagonal planes and connecting periodically to each other, consequently forming ladder-like structure, wherein the inner side of the fibrous nanocarbon is open and connected to the outer space.

Carbon hexagonal planes of said ladder-structured fibrous nanocarbon align as shown in Figures 1-3, for example, ladder-structured fibrous nanocarbons produced at 500°C in Example 1 have a tubular structure, wherein the carbon hexagonal planes align at 0.1 ~ 5 degree to the fiber axis, but the hexagonal plane stacking connected to each other at 15 nm intervals aligns perpendicular to the fiber axis.

Also, as shown in Figures 2 and 3, the inner space formed by connective units is open to outer space, and the alignment of carbon hexagonal planes is characterized by (1) angled alignment at 0.1 ~ 20

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degree to the fiber axis in the range of 2 ~ 80 nm the fiber cross-section width/thickness, and angled alignment at 20 ~ 85 degree to the fiber axis in the range of 80 ~ 800 nm the fiber cross-section width/thickness, and (2) the tendency that the each fibril cross-section width/thickness increases

5   according to increase of primary metal (active to carbon sources) content in the catalyst composition or increase of synthesis temperature.

Compared to ladder-structured fibrous nanocarbon in this invention as described above, conventional carbon nanotubes as prepared in Comparative Example 1 have relatively clean surface, and have no

10   separate parts even from high magnification observation, consequently being a unit body of thoroughly continuous inner space, as shown in SEM and TEM of Figures 5 and 6.

Preparation method of ladder-structured fibrous nanocarbon

15   Generally, supported catalysts, which are prepared by finely dispersing active metals on supports, are used for fibrous nanocarbon production wherein carbon source gases are pyrolyzed at prescribed temperatures by using said supported catalysts.

Supporting of catalysts such as transition metals is attained by strong

20   interaction of oxygen atom or heteroatom negative charge, or ion exchange principle. For example, iron nitrate or acetate containing oxygen of strong negative charge is dispersed on alumina, and reduced in hydrogen gas mixtures, resulting in active supported-metal catalyst.

Preparation method of ladder-structured fibrous nanocarbon in this

25   invention is similar with conventional methods in terms of using catalytic

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pyrolysis of gaseous or liquid carbon sources such as CO or hydrocarbons of 1 ~ 4 carbon atoms, but the catalyst is not a supported one but bulk metal or particulate metal catalyst.

Also, said bulk metal or particulate metal catalyst is necessary to experience segregation process by roles of hydrogen or hydrogen radical during the catalyst reduction process, to be formed as very fine metal particles.

To prepare more uniform fine metal particles, transition metals such as Fe, Ni or Co active to said carbon sources are used as primary metals, with 5 ~ 95wt% addition of secondary metals inactive to said carbon sources in order to assist fine-particle formation, providing uniformly finer metal particles, which are used as unsupported metal catalysts in this invention.

Specifically, in the case of using iron catalyst which shows high carbon yield from carbon monoxide in prescribed gas mixture composition at prescribed temperatures, in order to separate bulk or powdered iron particles finer through reduction process, metals such as Mn, Mo, Cr, W, and Ni which show no carbon yield from carbon monoxide are added 5 ~ 95wt% as secondary metals for fine dispersion of iron particles, providing alloy catalysts which are used as fibrous nanocarbon preparation catalysts. In use of ethylene as a carbon source, metals such as Co and Ni which show high carbon yield from ethylene in prescribed gas mixture composition at prescribed temperatures are used as primary metals, and metals such as Fe, Mn, Mo, Cr, and W at addition of 5 ~ 95wt% which show no carbon yield from ethylene are effective as secondary metals for dispersion of primary

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metals.

In a specific embodiment, for the preparation of cobalt-molybdenum (Co-Mo) catalyst, certain amounts of cobalt nitrate and ammonium molybdate aqueous solutions are first prepared. For the preparation of well dispersed Co-Mo catalyst, excess amounts of ammonium bicarbonate or oxalic acid must be added into the mixed solutions for obtaining the precipitate of mixed metal carbonates. The obtained mixed metal carbonates must be fully dried in vacuum at 80°C for over 8 h after filtering and rinsing. The obtained mixed metal carbonates are calcined for 2□10 h at 400°C under the air atmosphere for obtaining mixed metal oxides. The obtained Co-Mo oxides are first reduced for 0.5 ~ 40 h at the temperature ranges of 450 ~ 550°C under the hydrogen-helium mixed gases of certain ratios. Specifically, the volume percentage of hydrogen should be 1~40 to the volumes of helium. After the first reduction, obtained Co-Mo alloy should be cooled to room temperature for the passivation of the surface with the appropriate oxidation conditions. For the passivation, the desirable amounts oxygen to nitrogen and period are 0.5~10 volume percent and 10~120 min, respectively. The obtained Co-Mo alloy metal contains the compositions of cobalt 80~99 weight percents, more desirably 85~95 weight percents. Mo compositions are not completely reduced, containing oxygen less than 0.01~90 percents over the 1 weight percent of Mo.

If the compositions of cobalt in Co-Mo catalyst is more than 99 %, the prepared fibrous nanocarbons contains some of different structured carbons or showed the values of aspect ratio (length of fibrous

nanocarbon/width of fibrous nanocarbon) less than 20.

For the preparation of fibrous nanocarbons using aforementioned Co-Mo catalyst, Co-Mo catalyst must be second reduced for 0.5 – 12 h at the temperature ranges of 450~550°C under the hydrogen-helium mixed gases of certain ratios. Specifically, the volume percentage of hydrogen should be 5~40 to the volumes of helium. If the temperature and period for the second reduction are shorter or lower than 0.5 h or 450°C, Co metal shows none or very low activity to the carbon source for the fiber growth. If the temperature and period for the second reduction are longer or higher than 12 h or 550°C, a severe sintering of separated Co metal occurs, resulting in very heterogeneous structures and dimensions of fibrous nanocarbons.

For the preparation of the fibrous nanocarbons using Co-Mo catalyst, a certain amounts of catalysts put on the quartz boat or plate, and then the boat or plate located at the center of the reaction tube for the contacting of carbon containing gases at prescribed reaction temperature and period. In addition to the above-mentioned method and fibrous nanocarbons produced thereby this invention also concerns a method for producing a substantially uniform plurality of essentially ladder-structured or paired, discrete fibrous nanocarbons which comprises contacting for an appropriate period of time and at a suitable pressure, suitable metal-containing particles with a suitable gaseous, carbon-containing gas, at a temperature between about 380°C and 750°C. The mixture of ethylene, carbon monoxide and hydrogen are introduced by the exact control of flow rate with mass flow

controller. The desirable flow rate and partial pressure of carbon containing gas are 0.5~30 sccm per 1 mg of catalyst and 10~95% of carbon containing gas, respectively. For obtaining the ladder-structured fibrous nanocarbon, the addition of 1~50 volume% of carbon monoxide per ethylene to carbon

5   containing gas are desirable. The period for the reaction is 2 min ~ 48 h.

The ladder-structured fibrous nanocarbon and the pair-structured fibrous nanocarbon prepared in this invention have clearly different structures with bamboo-like structure, showing the width of 2.0 – 800 nm and open knobs in every 5 – 100 nm in inner side of fibrous nanocarbons,

10   and relatively developed graphitic structure which are very suitable as fillers for the applications of transparent conductive materials, transparent or non-transparent electromagnetic shielding materials, high thermal or electric conductive materials, anodic or conductive materials of lithium or air secondary batteries, electrodic materials for EDLC, and catalyst supports

15   for the fuel cells and organic unit reactions.

This invention is illustrated in the examples and comparative examples which follow. The examples or comparative examples are set forth to aid in an understanding of the invention but are not intended to, and should not be construed to limit in any way the invention as set forth in the

20   claims which follow thereafter.

EXAMPLES

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In all examples and comparative examples which follow, the symbol '%' means weight percentage if there are no description.

The preparation of ladder-structured fibrous nanocarbons

Example 1

5   For the preparation of the ladder-structured fibrous nanocarbons, cobalt-molybdenum (Co-Mo, Co/Mo = 9/1 (wt/wt)) catalyst was prepared as follows. The mixture of the adequate amounts of cobalt nitrate and ammonium molybdenum was dissolved in 200 ml distilled water, and excess amounts of ammonium bicarbonate was added slowly, the mixture

10   being stirred for 30 min. The obtained mixed metal precipitate was fully dried in vacuum at 80°C for over 8 h after filtering and rinsing with distilled water twice. The obtained mixed metal carbonates are calcined for 5 h at 400°C under the air flow of 200sccm for obtaining mixed metal oxides. The obtained Co-Mo oxides are first reduced for 0.5 h at the temperature ranges

15   of 500°C under the hydrogen-helium mixed gases of certain ratios. Specifically, the volume percents of hydrogen were 10 to the total volume. After the first reduction, obtained Co-Mo alloy was cooled to room temperature for the passivation of the surface with the appropriate oxidation conditions. For the passivation, the desirable amounts oxygen to nitrogen

20   and period are 5 volume percent and 30 min, respectively. The obtained Co-Mo alloy metal contains the compositions of cobalt 89.4 weight percents.

For the preparation of fibrous nanocarbons using aforementioned

Co-Mo catalyst, 30 mg of Co-Mo catalyst was second reduced for 2 h at 480°C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume).

For the preparation of the fibrous nanocarbons using Co-Mo catalyst, 5   30mg of second reduced Co-Mo catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of carbon containing gases at 500°C with a carbon containing gas (carbon monoxide/Ethylene/hydrogen = 25/50/25 vol ratios; total flow rate 200sccm) for 1 h. After reaction, 934 mg of ladder-structured fibrous nanocarbon was 10 obtained.

Graphitization properties of the fibrous nanocarbons were analyzed in X-ray diffraction (Rigaku Geigerflex II; CuKα, 40KV, 30mA, Stepwise Method) at 2θ 5 ~ 90°. From the diffraction, the average (002) plane interlayer spacing (d002, hereinafter) and the average stacking height of 15 (002) planes (Lc (002), hereinafter) were obtained according to the JSPS procedure (The 117th committee in Japan society for the promotion of science. *Tanso*, 36, 25-34 (1963)).

The surface areas of the fibrous nanocarbons were calculated by using the Dubinin equation from the nitrogen isotherm at -190°C.

20   Table 1 shows d002, Lc (002), and the surface areas of the fibrous nanocarbons produced in corresponding examples.

The morphology and structure of fibrous nanocarbons produced

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above were examined under a high resolution scanning electron microscope (HR-SEM, Jeol, JSM 6403F) and a transmission electron microscope (TEM, Jeol, JEM 2010F) as shown in Figures 1□3.

The fibrous nanocarbons as prepared above shows a composed structure of two unit tubular carbon nanofibers wherein the hexagonal planes align angled to the fibrous nanocarbon axis (the angle 0.1 ~ 5°), distinct from carbon nanotube as described above. Two unit carbon nanofibers are bridged periodically with carbon plane knobs by around 15 nm distant, forming ladder structure.

The average diameters or widths of the fibrous nanocarbons were measured by observation of 300 thousand magnified images through SEM monitor in random selection of 500 fibrous nanocarbons. The average diameter of the fibrous nanocarbon produced above was 23nm and 75% of fibrous nanocarbons ranged 12 ~ 32 nm diameters. The aspect ratio of the fibrous nanocarbon produced above was more than 200.

Examples 2 below illustrate production of fibrous nanocarbons under the same or different conditions over the same or different catalysts, and average diameters, d002, Lc(002), and surface areas of fibrous nanocarbons produced in corresponding Examples or Comparative examples are summarized in Tables 1 and 2, comparing with the comparative examples.

Example 2

For the preparation of fibrous nanocarbons using aforementioned Co-Mo catalyst, 30 mg of Co-Mo catalyst was second reduced for 2h at 550°C under the hydrogen-helium mixed gases (The partial pressure of
5   hydrogen is 20 volume % to the total volume).

For the preparation of the fibrous nanocarbons using Co-Mo catalyst, 30mg of second reduced Co-Mo catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of carbon containing gases at 550.degree. C with a carbon containing gas
10 (carbon monoxide/Ethylene/hydrogen = 25/50/25 vol ratios; total flow rate 200sccm) for 1 h. After reaction, 1328 mg of ladder-structured fibrous nanocarbon was obtained.

Table 1 shows d002, Lc (002), the surface areas and average width or breadth of the fibrous nanocarbons produced in corresponding example.

15 The fibrous nanocarbons as prepared above shows a composed structure of two unit tubular carbon nanofibers wherein the hexagonal planes align angled to the fibrous nanocarbon axis (the angle 0.1 ~ 5°), distinct from carbon nanotube as described above. Two unit carbon nanofibers are bridged periodically with carbon plane knobs by around 15
20 nm distant, forming ladder structure.

The average diameters or widths of the fibrous nanocarbons were measured by observation of 300 thousand magnified images through SEM

monitor in random selection of 500 fibrous nanocarbons.

Comparative example 1

Carbon Black(CB)-supported Fe/Ni mixture or alloy (6/4 w/w) catalyst

5   was prepared as follows. The mixture of the adequate amounts of iron nitrate and nickel nitrate was dissolved in 200 ml distilled water, and then CB (Table 1) 80 g was added to the solution, the mixture being stirred for 30 min.

The slurry was dried in a rotary evaporator at 80°C under 40 Torr,

10   providing a CB-supported Fe/Ni (6/4) catalyst (5% metal content per CB).

CB-supported Fe/Ni(6/4) as prepared above (110 mg) was dispersed in a quartz tray (length:width:thickness= 10:2.5:1.5 / mm (outer)), and then the tray was placed in the middle of a quartz tube (45 mm inner diameter), which was equipped with a conventional furnace. After He flow at ambient

15   temperature for 30 min, the gas mixture of 200sccm hydrogen/helium (20% hydrogen partial pressure) was introduced at 650°C for 2 h, and then the reaction was performed under 200sccm gas flow composed of a 75:25 carbon monoxide:hydrogen (v/v) mixture at 650°C for 2 h, providing 220 mg product involving carbon nanotubes (tubular carbon nanofibers) and CBs.

20   Table 1 shows d002, Lc(002), the surface areas and the average diameter of the carbon nanotube produced in corresponding examples.

The morphology and structure of carbon nanotube produced above were examined under a high resolution scanning electron microscope (HR-SEM, Jeol, JSM 6403F) and a transmission electron microscope (TEM, Jeol, JEM 2010F) as shown in Figures 5 and 6.

5   The carbon nanotubes as prepared above shows a tubular structure wherein the hexagonal planes align angled to the fibrous nanocarbon axis (the angle below 5°), which is almost align along to the fiber axis.

Also, the carbon nanotubes have flat planes and continuous hollow cores therein as examined under high resolution scanning electron microscope. As observed by transmission electron microscope shown in Figure 6, the carbon nanotubes have circular cross sections, and the widths of the carbon nanotubes are smaller than those of the hollow cores. The aspect ratio which shows the fiber dimension is more than 100.

The average diameters or widths of the fibrous nanocarbons were measured by observation of 300 thousand magnified images through TEM monitor in random selection of 500 fibrous nanocarbons.

Comparative example 2

For comparison, 30 mg of Co-Mo catalyst in example 1 was second reduced for 2 h at 800°C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume) 30mg of second reduced Co-Mo catalyst put on the quartz boat, and then the boat

located at the center of the reaction tube for the contacting of carbon containing gases at 800°C with a carbon containing gas (carbon monoxide/hydrogen = 20/80 vol ratios; total flow rate 200sccm) for 2 h. After reaction, no carbon was deposited.

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Comparative example 3

For comparison, 30 mg of Co-Mo catalyst in example 1 was second reduced for 2 h at 350 degree C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume). 30mg of second reduced Co-Mo catalyst put on the quartz boat, and then the boat located at the center. of the reaction tube for the contacting of carbon containing gases at 350°C with a carbon containing gas (carbon monoxide/hydrogen = 20/80 vol ratios; total flow rate 200sccm) for 12 h. After reaction, no carbon was deposited.

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Comparative example 4

For comparison, 30 mg of Co-Mo catalyst in example 1 was second reduced for 2 h at 500°C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume). 30mg of second reduced Co-Mo catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of carbon containing gas (carbon monoxide = 100 vol ratios; total flow rate 200sccm)

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at 500.degree. C for 12h. After reaction, no carbon was deposited.

Comparative example 5

Catalyst of 30 mg prepared as in Example 1 was set in the furnace as described in Example 1. The reduction was performed in the gas mixture of 200 sccm hydrogen/helium (20v/v% hydrogen partial pressure) at 600°C for 2 h, and then the reaction was performed in the gas mixture of 200 sccm ethylene/hydrogen (80v/v% hydrogen partial pressure) at 600°C for 2 h, providing 1333 mg fibrous nanocarbons, which have no connection unit between fibrils.

Table 1

	X-ray diffraction properties		N_2 BET surface area (m^2/g)	Average width/thickness of fibrous nanocarbon (nm)
	d_{002} (nm)	Lc (002) (nm)		
Example 1	0.3422	4.4	308	22/26
Example 2	0.3401	6.7	330	108/46
C-example 1	0.3398	8.2	221	33/32

C-example 2	-	-	-	-
C-example 3	-	-	-	-
C-example 4	-	-	-	-
C-example 5	0.3489	3.5	210	110/77

The pair-structured fibrous nanocarbon

Figures 7 show the SEM photographs of the pair-structured fibrous nanocarbon of this invention. Low magnification can not discrete the combined structure of two unit carbon nanofibers because of low resolution, where the higher magnification can discrete the pair structure which is composed of two independently grown unit carbon nanofibers. Pair-structured fibrous nanocarbon illustrates the ribbon-like or hexagonal column as shown in Figures of 9 - 11. The width of cross-section decreases with increasing the preparation temperature. The hexagonal cross-section may be induced from the shape of active catalyst (ref: S. H. Yoon, A. Tanaka, S. Y. Lim, Y. Korai, I. Mochida, B. Ahn, K. Yokogawa, C. W. Park, 3-dimensional structure of carbon nanofiber; carbon nano rod, Proceedings of international symposium on carbon, 2003, Oviedo, Spain, 8-1, 76).

This invention discloses that such separated hexagonal shaped very fine metal catalyst is further divided into two particles with plane symmetry and independent two same carbon nanofibers are grown over the divided

catalyst particles. Two independently grown unit carbon nanofibers compose the pair-structured fibrous nanocarbon with the combination of two fiber units by the Van der Waals force.

Pair-structured fibrous nanocarbons in the present invention have
5   feather (herringbone), tubular, and columnar (platelet) structure whose carbon hexagonal planes are laminated at certain angles to the fiber axis, being formed by bonding of two ribbon- or plate-shape unit carbon nanofibers of trapezoidal cross section at regular distance by means of interaction between said two unit fibers, distinctly differing from conventional
10 carbon nanotubes which have general circular cross section which involves hollow core of a regular size with the concentric carbon hexagonal stacking.

Pair-structured fibrous nanocarbon of this invention concerns the uni-modally or bi-modally grown fibrous nanocarbons, which is characterized by (1) the sp^2 hybrid carbon content of more than 95% per
15 total content; (2) d_{002} of 0.3360nm~0.3800nm, the (002) plane stacking of more than 8 layers; (3) the width/thickness of fiber cross-section of 2.0 nm~800 nm, and the fiber thickness ranges 1.0 ~ 400 nm; (4) the aspect ratio is more than 20, (5) bonding of two unit carbon nanofibers with said (1) ~ (4) features at 0.4nm ~ 30nm distance by the interaction between the two
20 unit fibers (Van der Waals Force) in the beginning of fiber formation, (6)the hexagon-shaped cross section formed by two trapezoids as shown in Figures 7 ~ 11, (7) the width of 2.0 ~ 800 nm and the thickness of 2.0 ~ 800 nm in said cross section, (8) in pair-structured fibrous nanocarbon with said (1) ~ (7) features, the width/depth of unit fibers and the distance between

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two unit fibers depending on preparation temperatures and iron contents in preparation catalysts, and (9) with temperature decreasing, the width/depth of unit fibers decreasing but the distance between two unit fibers increasing. In Examples, more detailed description is given.

5   Carbon hexagonal plane alignment or texture in the pair-structured fibrous nanocarbon tends to depend on the texture of the unit fibers. As shown in Figures 7 ~ 10, the unit fiber at 600°C as prepared in Example 3 shows a platelet (columnar) texture where the carbon hexagonal planes align at angles of 75 ~ 90 degree to the fiber axis.

10   Pair-structured fibrous nanocarbon which is formed by bonding of two said unit fibers also shows platelet (columnar) texture. However, as shown in Figures 11 and 12, in the case of preparation of pair-structured fibrous nanocarbon at relatively low temperature such as 520oC as in Example 4, unit fibers which have the hexagonal alignment at 0.1 ~ 75 degree to the

15   fiber axis bond by two units by inter-particle force or Van der Waals force, resulting in pair-structured fibrous nanocarbons which appear to have herringbone (feather) structure. However, said pair-structured fibrous nanocarbon shows hexagon cross section originating from trapezoid-shaped cross section of said unit fibers, distinctly differing from

20   conventional herringbone carbon nanofibers with circular cross section.

The distance between two unit fibers which constitute the pair-structured fibrous nanocarbon is so small as 1 ~ 5 nm in preparation at high temperatures such as 600°C as in Example 3 as shown in Figure 10, but shows relatively large values of 5 ~ 20 nm in preparation at low

25   temperatures such as 520°C as in Example 4 as shown in Figure 12.

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Figure 13 illustrates a schematic model of pair-structured fibrous nanocarbon. As illustrated above, pair-structured fibrous nanocarbon in this invention is formed as a single body through bonding of two unit fibers by inter-fiber force or Van der Waals force, showing the inner side open to the

5   outer space, distinctly differing from conventional carbon nanotubes.

Also, in preparation at relatively high temperatures, pair-structured fibrous nanocarbon in this invention shows a hexagon shape of the cross section, where the unit fibers with trapezoid-shaped cross section are very close in the inter-fiber distance. Differing from pair-structured fibrous

10   nanocarbons prepared at high temperatures, pair-structured fibrous nanocarbons prepared at relatively low temperatures are found to show the cross section close to a regular hexagon and relatively large inter-fiber distance between two unit fibers.

Compared to pair-structured fibrous nanocarbon as described above,

15   multi-walled carbon nanotubes as prepared in Example 6 are shown in SEM and TEM of Figures 5 and 6. As shown in SEM image of Figure 5, carbon nanofibers have cleaner surface than pair-structured fibrous nanocarbon in this invention, and at a high magnification, a separation part as in this pair-structured fibrous nanocarbon is never found, which reflects that said

20   multi-walled carbon nanotubes are formed totally as a single unit body having a continuous hollow core. Furthermore, as shown in TEM image of Figure 6, carbon nanotubes have the feature that the size of wall comprising the stacking of carbon hexagonal planes is generally smaller than the size of inner hollow.

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Preparation method of pair-structured fibrous nanocarbon

Preparation method of pair-structured fibrous nanocarbon in this invention is similar with conventional methods in terms of using catalytic pyrolysis of gaseous or liquid carbon sources, but the catalyst is not a

5 supported one but bulk metal or particulate metal catalyst. Also, said bulk metal or particulate metal catalyst is necessary to experience segregation process by roles of hydrogen or hydrogen radical during the catalyst reduction process, to be formed as very fine metal particles. To obtain more uniform fine particles of said catalysts through said segregation process,

10 transition metals active to carbon sources, such as Fe, Ni or Co are used as primary metals, with 5 ~ 95wt% addition of secondary metals inactive to said carbon sources in order to assist fine-particle formation, providing unsupported metal catalysts for producing pair-structured fibrous nanocarbon in this invention.

15 Specifically, in the case of using iron catalyst which shows high carbon yield from carbon monoxide in prescribed gas mixture composition at prescribed temperatures, in order to separate bulk or powdered iron particles finer through reduction process, metals such as Mn, Mo, Cr, W, and Ni which show no carbon yield from carbon monoxide are added 5 ~

20 95wt% as secondary metals for fine dispersion of iron particles, providing alloy catalysts which are used as fibrous nanocarbon preparation catalysts.

In use of ethylene as a carbon source, metals such as Co and Ni which show high carbon yield from ethylene in prescribed gas mixture composition at prescribed temperatures are used as primary metals, and

25 metals such as Fe, Mn, Mo, Cr, and W at addition of 5 ~ 95wt% which show

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no carbon yield from ethylene are effective as secondary metals for dispersion of primary metals.

In the preparation of iron-manganese (Fe-Mn) catalyst, in order to obtain Fe-Mn solid solution or solid-solution-like alloy, respective aqueous
5   solutions of manganese nitrate or acetate and iron nitrate or acetate at prescribed amount are first prepared, and two said solutions at prescribed ratio are mixed at room temperature, and then ammonium bicarbonate or oxalic acid is added into said mixed solutions until the precipitate is formed.

The precipitate as prepared above (Fe-Mn carbonate or oxalate) must
10   be fully dried in vacuum at 80°C for over 8 h after filtering and rinsing by 2 times with 50°C distilled water and 1 time with ethyl alcohol. The precipitate dried is calcined for 2~10 h at 400oC under air in a horizontal or standing furnace, resulting in mixed metal oxides. The oxides prepared above are reduced for 0.5 ~ 40 h at the temperature ranges of 450 ~ 550oC
15   (preferably, 450 ~ 510°C)under gas mixture of 1 ~ 40 v/v% hydrogen (preferably, 5 ~ 30 v/v%) and nitrogen, or argon, or helium, resulting in Fe-Mn alloy catalyst.

Before exposure of Fe-Mn alloy catalyst as reduced above to the atmosphere, the passivation is performed under gas mixture containing
20   0.5~10v/v% oxygen in nitrogen, argon or helium for 10~120 min. In Fe-Mn catalysts, the Fe content is 5 ~ 95wt%, preferably 20 ~ 85wt%.

After reaction of Fe-Mn catalyst, the passivation is performed under gas mixture containing 1~5v/v% oxygen in nitrogen, argon or helium for 30 min. In Fe-Mn catalysts, the Fe content is 5 ~ 95wt%, preferably 20 ~
25   85wt%.

In more than 95wt% Fe content, two different structure carbon nanofibers can be formed in mixture, or the aspect ratio of said carbon nanofibers can be less than 20. In production of fibrous nanocarbons using said Fe-Mn catalysts, the reduction condition is the same with said catalyst
5   reduction condition, and the temperature and time are recommended as 450~550°C and 0.5 ~ 12 h, respectively.

Also, the reduction temperature of lower than 450°C or the reduction time of less than 30 min provide no fully-reduced catalyst to show no or little activity, and the reduction temperature of higher than 550°C or the
10   reduction time of more than 12 h lead to sintering of fine particles which have been formed by said segregation process during hydrogen reduction, consequently resulting in inactive catalyst for production of fibrous nanocarbons due to loss of independency.

Fe-Mn alloy catalysts as prepared above are dispersed on boat or
15   plate of alumina or silica, or are set in a floating or flow furnace, and the CO/hydrogen mixture of 0.5 ~ 30 sccm per 1 mg catalyst (preferably, 1 ~ 10 sccm) is introduced to said furnace for prescribed time, providing pair-structured fibrous nanocarbon, wherein said gas mixture contains 10 ~ 95v/v% hydrogen partial pressure, the temperature is proper at 380 ~ 750°C
20   (preferably, 520 ~ 700°C), and the time is proper for 2 min ~ 48 h (preferably, 20 min ~ 24 h).

As described in Examples below, in the case of introduction of the CO/hydrogen mixture of 3.3 sccm per 1 mg catalyst (25v/v% hydrogen partial pressure) for 2 h, the pair-structured fibrous nanocarbon can be
25   produced at high yields of 1.5 ~ 60 times per catalyst weight depending on

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production conditions, the reaction for 8 h providing the carbon yield of 30 times per catalyst weight.

As pyrolytic amorphous carbons such as pyrocarbon are hardly formed on the surface of pair-structured fibrous nanocarbon, the

5   pair-structured fibrous nanocarbon comprising two unit fibers with very clean surface can be attained.

The reaction temperatures of higher than 750°C lead however to the deactivation of catalyst, producing almost no fibrous nanocarbon. Also, the reaction time of less than 30 min provides very small yield which is not

10   economical, and the reaction time of more than 48 h shows no further yield increase, rather undesirably inducing aggregation of fibers produced and decreasing independency of individual fibers.

Pair-structured fibrous nanocarbon in this invention shows 2.0 ~ 800 nm fiber diameters and 0.5 ~ 30 nm inter-unit fiber distances, and also has

15   the relatively developed graphitic structure depending on the reaction temperature, being expected for various applications as aforementioned in Examples 1 and 2.

The following Examples 3 ~ 6 provide detailed description of pair-structured fibrous nanocarbon in the present invention.

20

Example 3

For the preparation of the pair-structured fibrous nanocarbons, iron-manganese (Fe-Mn, Fe/Mn = 3/7 (wt/wt)) catalyst was prepared as

follows. The mixture of the 5.0g and 29.0 g of iron nitrate and manganese nitrate was dissolved in 200 ml distilled water, and an excess amount of ammonium bicarbonate was added slowly, the mixture being stirred for 30 min. The obtained mixed metal precipitate was fully dried in vacuum at 80

5   degree C for over 8 h after filtering and rinsing with distilled water twice. The obtained mixed metal carbonates are calcined for 5 h at 400°C under the air flow of 200sccm for obtaining mixed metal oxides. The obtained Fe-Mn oxides are first reduced for 0.5 h at the temperature ranges of 500 degree C under the hydrogen-helium mixed gases of certain ratios. Specifically, the

10 volume percents of hydrogen were 10 to the total volume. After the first reduction, obtained Fe-Mn alloy was cooled to room temperature for the passivation of the surface with the appropriate oxidation conditions. For the passivation, the desirable amounts oxygen to nitrogen and period are 5 volume percent and 30 min, respectively. The obtained Fe-Mn alloy metal

15 contains the compositions of cobalt 89.4 weight percents.

For the preparation of fibrous nanocarbons using aforementioned Fe-Mn catalyst, 30 mg of Fe-Mn catalyst was second reduced for 2 h at 480 degree C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume(100sccm)).

20   For the preparation of the fibrous nanocarbons using Fe-Mn catalyst, 30mg of second reduced Fe-Mn catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of with a carbon containing gas (carbon monoxide/hydrogen = 20/80 vol ratios; total flow rate 200sccm) at 600.degree. C for 1 h. After reaction, 622 mg of

pair-structured fibrous nanocarbon was obtained.

Graphitization properties of pair-structured fibrous nanocarbons were analyzed in X-ray diffraction (Rigaku Geigerflex II; CuKα, 40KV, 30mA, Stepwise Method) at 2θ 5 ~ 90°. From the diffraction, the average (002)
5   plane interlayer spacing (d002, hereinafter) and the average stacking height of (002) planes (Lc(002), hereinafter) were obtained according to the JSPS procedure (Otani Sugio, et al. Carbon Fibers. Nihon Kindaihensyusya; Tokyo, 1983). The surface areas of the fibrous nanocarbons were calculated by using the Dubinin equation from N2 BET isotherms. Table 2
10 shows d002, Lc (002), the surface areas and the width/thickness of the fibrous nanocarbons produced in corresponding examples.

The morphology and structure of fibrous nanocarbons produced above were examined under a high resolution scanning electron microscope (HR-SEM, Jeol, JSM 6403F) and a transmission electron
15 microscope (TEM, Jeol, JEM 2010F) as shown in Figures 7 - 10.

The pair-structured fibrous nanocarbons as prepared above shows a composed structure of two unit platelet carbon nanofibers wherein the hexagonal planes align angled to the fibrous nanocarbon axis (the angle 85 ~ 89°), distinct from carbon nanotube as described above. Two unit carbon
20 nanofibers are combined by Van der Waals force, forming pair structure.

Carbon hexagonal planes were found to align almost perpendicular to the fiber axis, and the cross section of the fibers was found to shape a hexagon as shown in the scanned profile of scanning tunneling microscope

of Figure 9. As shown in Figure 10, the width of the fibers shapes oblong trapezoid where the side and front shape of the fibers are different. The front observation does not show bonding of two unit fibers, but the side observation shows the single fiber formation from two plate-shaped unit

5   fibers of trapezoidal cross section. The aspect ratio which shows the fiber dimension is more than 80.

The average diameters or widths of the fibrous nanocarbons were measured by observation of 300 thousand magnified images through SEM monitor in random selection of 500 fibrous nanocarbons.

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Example 4

For the preparation of the pair-structured fibrous nanocarbons using aforementioned Fe-Mn catalyst, 30 mg of Fe-Mn catalyst was second reduced for 2 h at 480 degree C under the hydrogen-helium mixed gases

15 (The partial pressure of hydrogen is 20 volume % to the total volume(200sccm)).

For the preparation of the fibrous nanocarbons using Fe-Mn catalyst, 30mg of second reduced Fe-Mn catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of with

20 a carbon containing gas (carbon monoxide/hydrogen = 20/80 vol ratios; total flow rate 200sccm) at 520.degree. C for 1 h. After reaction, 228 mg of pair-structured fibrous nanocarbon was obtained.

Table 2 shows d002, Lc (002), the surface areas and the width/thickness of the fibrous nanocarbons produced in corresponding examples.

The morphology and structure of fibrous nanocarbons produced
5   above were examined under a high resolution scanning electron microscope (HR-SEM, Jeol, JSM 6403F)' and a transmission electron microscope (TEM, Jeol, JEM 2010F) as shown in Figures 11 and 12.

The pair-structured fibrous nanocarbons as prepared above shows a composed structure of two unit platelet carbon nanofibers wherein the
10   hexagonal planes align angled to the fibrous nanocarbon axis (the angle 85 ~ 89°), distinct from carbon nanotube as described above. Two unit carbon nanofibers are combined by Van der Waals force, forming pair structure.

The average diameters or widths of the fibrous nanocarbons were measured by observation of 300 thousand magnified images through SEM
15   monitor in random selection of 500 fibrous nanocarbons.

The inter-spacing between the two unit carbon nanofibers shows 4.2 nm as shown in Figure 10.

Example 5

20   For the preparation of the pair-structured fibrous nanocarbons using aforementioned Co-Mo catalyst in Example 1, 30 mg of Co-Mo catalyst was

second reduced for 2 h at 480 degree C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume(100sccm)).

For the preparation of the fibrous nanocarbons using Co-Mo catalyst, 30mg of second reduced Co-Mo catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of with a carbon containing gas (ethylene/hydrogen = 75/25 vol ratios; total flow rate 200sccm) at 520.degree. C for 2 h. After reaction, 1170 mg of pair-structured fibrous nanocarbon was obtained.

Table 2 shows d002, Lc (002), the surface areas and the width/thickness of the fibrous nanocarbons produced in corresponding examples.

The pair-structured fibrous nanocarbons as prepared above shows a composed structure of two unit platelet carbon nanofibers wherein the hexagonal planes align angled to the fibrous nanocarbon axis (the angle 85 ~ 89°), distinct from carbon nanotube as described above. Two unit carbon nanofibers are combined by Van der Waals force, forming pair structure.

The average diameters or widths of the fibrous nanocarbons were measured by observation of 300 thousand magnified images through SEM monitor in random selection of 500 fibrous nanocarbons.

The inter-spacing between the two unit carbon nanofibers shows 2.7 nm.

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Example 6

For the preparation of the pair-structured fibrous nanocarbons using aforementioned Co-Mo catalyst in Example 1, 30 mg of Co-Mo catalyst was second reduced for 2 h at 480 degree C under the hydrogen-helium mixed

5   gases (The partial pressure of hydrogen is 20 volume % to the total volume(100sccm)).

For the preparation of the fibrous nanocarbons using Co-Mo catalyst, 30mg of second reduced Co-Mo catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of with

10   a carbon containing gas (ethylene/hydrogen = 75/25 vol ratios; total flow rate 200sccm) at 600.degree. C for 1 h. After reaction, 133 mg of pair-structured fibrous nanocarbon was obtained.

Table 2 shows d002, Lc (002), the surface areas and the width/thickness of the fibrous nanocarbons produced in corresponding

15   examples.

The pair-structured fibrous nanocarbons as prepared above shows a composed structure of two unit platelet carbon nanofibers wherein the hexagonal planes align angled to the fibrous nanocarbon axis (the angle 85 ~ 89°), distinct from carbon nanotube as described above. Two unit carbon

20   nanofibers are combined by Van der Waals force, forming pair structure.

The average diameters or widths of the fibrous nanocarbons were measured by observation of 300 thousand magnified images through SEM

monitor in random selection of 500 fibrous nanocarbons. The inter-spacing between the two unit carbon nanofibers shows 5.8 nm.

Comparative example 6

5   For comparison, 30 mg of Fe-Mn catalyst in example 1 was second reduced for 2 h at 800°C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume). 30mg of second reduced Fe-Mn catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of carbon 10   containing gases at 800°C with a carbon containing gas (carbon monoxide/hydrogen = 20/80 vol ratios; total flow rate 200sccm) for 2 h. After reaction, no carbon was deposited.

Comparative example 7

15   For comparison, 30 mg of Fe-Mn catalyst in example 3 was second reduced for 2 h at 350°C under the hydrogen-helium mixed gases (The partial pressure of hydrogen is 20 volume % to the total volume). 30mg of second reduced Fe-Mn catalyst put on the quartz boat, and then the boat located at the center of the reaction tube for the contacting of carbon 20   containing gas (The partial pressure of hydrogen is 80 volume % to the total volume) at 350°C for 12 h. After reaction, no carbon was deposited.

Comparative example 8

30 mg of Catalyst as in Example 3 (Fe/Mn 3/7) was set in the middle of a quartz tube (45 mm inner diameter) in the horizontal furnace as used in catalyst preparation, and the mixture of 200sccm hydrogen/helium (20v/v% hydrogen partial pressure) was flowed at 500°C for 2 h on purpose of catalyst reduction, and then the reaction was performed at 480°C for 12 h, providing almost no pair-structured fibrous nanocarbon.

Comparative example 9

30 mg of Catalyst as in Example 3 (Fe 100%) was set in the middle of a quartz tube (45 mm inner diameter) in the horizontal furnace as used in catalyst preparation, and the mixture of 200sccm hydrogen/helium (20v/v% hydrogen partial pressure) was flowed at 600°C for 2 h on purpose of catalyst reduction, and then the boat located at the center of the reaction tube for the contacting of carbon containing gases at 600°C with a carbon containing gas (carbon monoxide/hydrogen = 20/80 vol ratios; total flow rate 200sccm) for 2 h. After reaction, 1440mg of carbon nanofibers were deposited with platelet structure of unit carbon nanofibers.

Table 2

	X-ray diffraction properties		N_2 BET surface area (m^2/g)	Average width/thickness of fibrous nanocarbon (nm)
	d_{002}(nm)	Lc (002)(nm)		
Example 3	0.3360	24.4	108	144/48
Example 4	0.3392	8.4	230	32/28
Example 5	0.3411	5.7	255	19/16
Example 6	0.3382	6.4	239	33/27
C-example 6	-	-	-	-
C-example 7	-	-	-	-
C-example 8	-	-	-	-
C-example 9	0.3363	22.9	92	150/83

Industrial Applicability

The ladder and pair-structured fibrous nanocarbons in this invention, which is different from conventional filamentous carbons, carbon nanofibers and carbon nanotubes, have open structure. Therefore, the fibrous

nanocarbon of this invention is expected as a superior material for practical applications such as transparent conductive composites; transparent electromagnetic shields; lithium secondary battery, EDLC(Electric Double Layered Capacitor), and air cells; catalyst supports for fuel cells or organic

5   reactions; electrification blocks for solar cells; electric desalination electrodes; gas storage; isotope separator; and removal of SO_x or NO_x.